

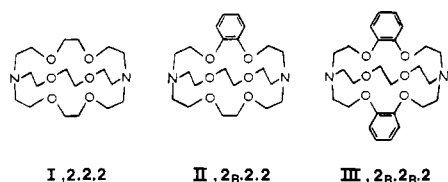
Formation and Dissociation Kinetics of Alkaline-Earth Ions with Benzo-Substituted Cryptands

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The formation and dissociation rate constants of Ca^{2+} , Sr^{2+} , and Ba^{2+} complexes of cryptands $2_{\text{B}}.2.2$ and $2_{\text{B}}.2_{\text{B}}.2$ have been measured in water as a function of temperature. The proton-catalyzed dissociation rate constants have also been determined. The introduction of the benzo rings causes a progressive decrease of the formation rate constants. The dissociation rate constants for the Ca cryptates remain almost constant while those for the Sr and Ba cryptates increase by factors of ~ 6 and ~ 800 , respectively, going from $2.2.2$ to $2_{\text{B}}.2_{\text{B}}.2$. The complexation selectivity changes from $\text{Ba}^{2+} > \text{Sr}^{2+} \gg \text{Ca}^{2+}$ for $2.2.2$ and $2_{\text{B}}.2.2$ to $\text{Sr}^{2+} \gtrsim \text{Ba}^{2+} > \text{Ca}^{2+}$ for $2_{\text{B}}.2_{\text{B}}.2$. All complexes undergo first-order proton-catalyzed dissociation with $k_{\text{obsd}} = k_{\text{d}} + k_{\text{H}}[\text{H}^+]$. The proton catalysis rate constants, k_{H} , follow the same pattern as the uncatalyzed dissociation rate constants, k_{d} ; however, the ratio $k_{\text{H}}:k_{\text{d}}$ decreases in the sequence $\text{Ca} > \text{Sr} > \text{Ba}$.

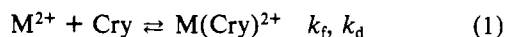
The macrobicyclic polyoxadiazines, cryptands, synthesized by Lehn and co-workers^{2,3} form stable complexes with alkali-metal, alkaline-earth, and post-transition-metal cations.⁴⁻⁶ The high degree of complexation selectivity exhibited by these ligands for certain cations or groups of cations is related to structural factors such as (i) cavity size, (ii) number and type of donor atoms, and (iii) ligand thickness.⁷ The introduction of benzo rings into the bridging polyether strands of the unsubstituted cryptand $2.2.2$ (I) results in cryptands $2_{\text{B}}.2.2$ (II)



and $2_{\text{B}}.2_{\text{B}}.2$ (III). The addition of the benzo rings has a pronounced effect on monovalent/bivalent cation selectivity,⁸ monovalent ion complexation kinetics in methanol^{9,10} and propylene carbonate,¹¹ and transfer activity coefficients between water and methanol.¹² Generally, the benzo-cryptate complexes have smaller stability constants^{8,13-15} and slower formation rates and faster dissociation rates⁹⁻¹¹ and the ligands are less extensively hydrated¹² than the unsubstituted cryptand, $2.2.2$ (I). This has been attributed to the combined effects of decreased cavity size, weaker catechol-type oxygen donor atoms, and increased thickness and hydrophobicity of the benzo

cryptands. The benzo rings also provide a site convenient for the attachment of other functional groups¹⁶ or for incorporation into polymeric networks.^{17,18} These functionalized benzo cryptands have applications in ion chromatography,¹⁸⁻²⁰ in isotope separation,²¹ and as NMR reagents.²² Cryptand $2_{\text{B}}.2.2$ has been shown to affect the action potential and fast sodium ion current in cardiac Purkinje fibers, suggesting that the cryptand acts as a Na^+ or K^+ ionophore.²³

Previous kinetic studies of alkaline-earth ions with aliphatic cryptands revealed that complex formation rates are much slower than expected on the basis of the water exchange rates of the cations and that changes in both the formation and dissociation rates are responsible for the complexation selectivity pattern.²⁴ The present study reports on the formation and dissociation kinetics (eq 1) at high pH of cryptands (Cry) $2_{\text{B}}.2.2$ and $2_{\text{B}}.2_{\text{B}}.2$ with alkaline-earth cations (M^{2+}) Ca^{2+} , Sr^{2+} , and Ba^{2+} and on the acid-catalyzed dissociation of the respective cryptates.²⁵



Experimental Section

Materials. The cryptands were obtained from E. Merck Laboratories or PCR, Inc., and used without further purification. Aqueous solutions of the ligand were prepared by weight and standardized by potentiometric titration with acid or spectrophotometric titration with standard lead perchlorate. The metal salts used either were ultrapure chlorides (Aldrich) or were prepared by the action of HCl on ultrapure carbonates (Aldrich). Tetramethylammonium hydroxide (J. T. Baker) or tetraethylammonium hydroxide (Aldrich) was used to adjust the

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- (25) Cox, B. G.; van Truong, N.; Schneider, H. *J. Am. Chem. Soc.* **1984**, *106*, 1273-1280. This article appeared after acceptance of our article. Values of k_{d} in H_2O are in excellent agreement with the present values. Values of k_{f} were obtained from $k_{\text{f}} = k_{\text{d}}K_{\text{s}}$ and are in good agreement with present values except for complexes of Ca and Sr with $2_{\text{B}}.2_{\text{B}}.2$, where the agreement is only fair.

pH and, after neutralization with HCl, to control the ionic strength. All solutions were prepared with deionized or doubly distilled water that was freshly boiled and cooled in the absence of CO₂ just prior to use.

Spectral Measurements. Spectra of the cryptands and their metal ion complexes were recorded with a Hitachi 100-80, Cary 14, or Beckman 24 double-beam spectrophotometer. Spectrophotometric titrations were carried out by preparing solutions containing a fixed amount of cryptand ($(5-10) \times 10^{-5}$ M) at pH 11.0 and varying amounts of the metal chloride salt.

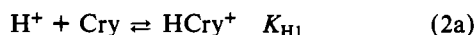
Kinetic Measurements. Reaction rates were measured on a Durrum D-130 stopped-flow, Hitachi 100-80, Beckman 24, or Cary 14 spectrophotometer. Reactions were monitored by recording absorbance changes in the ultraviolet region as a function of time. Stopped-flow traces were recorded on a storage oscilloscope and photographed or digitized and transferred to a microcomputer (Cromemco Z2D or an OLIS system). The temperature of the observation cell was maintained (± 0.1 °C) with a circulating constant-temperature bath. All reactions were first order, and the data were treated by standard least-squares procedures.

Formation rates were measured on the stopped-flow instrument at pH 11.0–11.5 at 0.1 M ionic strength with use of tetramethyl-(2_B.2.2) or tetraethylammonium chloride (2_B.2_B.2) as the supporting electrolyte. Reactions were monitored at 220–230 (2_B.2.2) or 269–279 nm (2_B.2_B.2). The reactions were initiated by mixing a solution of the cryptand ($(0.5-2.0) \times 10^{-4}$ M) with an equal volume of metal ion ($(0.5-25.0) \times 10^{-3}$ M). All reactions were studied at four or five temperatures covering a range from 6.0 to 45.0 °C. The uncatalyzed dissociation rates were measured at pH 11.0–11.5 with use of various scavenger species to force the reactions to completion. For the studies of the dissociation of the 2_B.2.2 cryptates, K⁺ and Na⁺ were used as scavengers for the free ligand and 2.2.2 was used as a scavenger for Sr²⁺ or Ba²⁺. The observed rate constants were independent of the nature of the scavenger and of the concentrations of K⁺ (0.063–0.482 M), Na⁺ (0.02–0.04 M), cryptand ($(2.3-7.5) \times 10^{-5}$ M), and metal ion (Ca²⁺, $(0.26-12.0) \times 10^{-3}$ M; Sr²⁺, $(2.4-7.5) \times 10^{-4}$ M; Ba²⁺, $(2.4-6.9) \times 10^{-4}$ M). The reactions were monitored at 222 (K⁺) or 274–282 nm (Na⁺ or 2.2.2). All reactions were studied at five or six temperatures over the range 14.0–60.0 °C. The dissociation of Sr(2_B.2_B.2)²⁺ was studied with use of 2.2.2 as the scavenger for Sr²⁺. Na⁺ and 2.2.1 were employed as scavengers of free 2_B.2_B.2 and Ca²⁺, respectively, for the dissociation of Ca(2_B.2_B.2)²⁺. The rate constants were independent of the nature of the scavenger and the concentration of 2_B.2_B.2 ($(0.75-1.50) \times 10^{-4}$ M), scavenger ($(4.0-5.0) \times 10^{-3}$ M, 2.2.2; 4.4×10^{-3} M, 2.2.1; 0.022 M, Na⁺), and metal ion ($(1.4-1.5) \times 10^{-4}$ M, Sr²⁺; $(2.9-5.8) \times 10^{-4}$ M, Ca²⁺). The dissociation rate constants for Ba(2_B.2_B.2)²⁺ were obtained from the intercepts of plots of k_{obsd} vs. [H⁺] except at 25 °C, where 2.2.2 ($(0.9-3.5) \times 10^{-3}$ M) was used as a scavenger for Ba²⁺. The reactions were monitored at $\lambda = 277-282$ nm. All reactions were studied at four or five temperatures from 15.0 to 35.0 °C. The acid-catalyzed dissociation rates of 2_B.2.2 and 2_B.2_B.2 cryptates were measured by mixing a solution of the preformed cryptate with an equal volume of a solution of known H⁺ concentration ($(2.0-50.0) \times 10^{-3}$ M) at an ionic strength of 0.10 M (HCl–Et₄NCl). The reactions were monitored at $\lambda = 274-276$ nm. All reactions were studied at four or five different temperatures from 10.2 to 37.0 °C.

Results

Spectral Properties and Protonation Constants. The presence of the catechol moiety in the bridges of the cryptands provides a chromophore that is sensitive to protonation and complexation with divalent cations. Complexation with Na⁺ (or K⁺) does not produce large spectral changes as shown in Figure 1. Thus Na⁺ and K⁺ may be used as scavengers for the study of the uncatalyzed dissociation reactions at high pH.

The stepwise protonation of the bridgehead tertiary amine nitrogen atoms is represented by eq 2a and 2b. The pro-



tonation constants of 2_B.2.2 were determined by potentiometric titration of 2.4×10^{-3} M cryptand with 0.010 M HCl at 25 °C at an ionic strength of 0.1 M (Et₄NCl). The values ob-

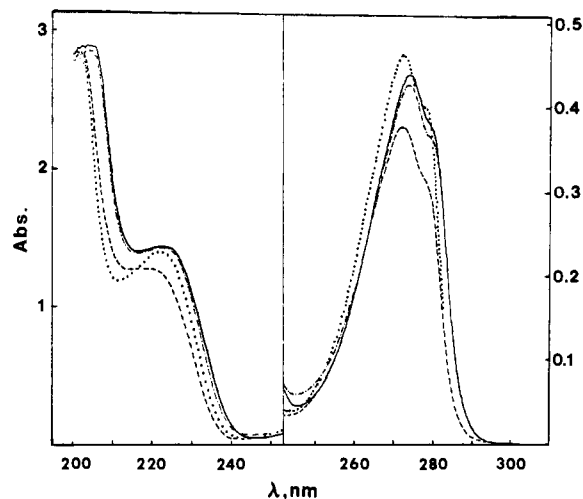


Figure 1. UV spectra of the cryptand 2_B.2_B.2 (8.5×10^{-5} M; 1-cm cells, reference solution water): (—) at pH 11.5; (···) at pH 3.0; (---) with 1.07×10^{-4} M SrCl₂, at pH 11.5; (-·-) with 1.0×10^{-2} M NaCl, at pH 11.5.

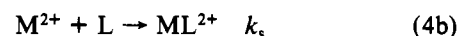
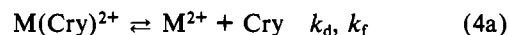
tained by analysis of the titration data gave $\log K_{\text{H1}} = 9.8$ and $\log K_{\text{H2}} = 6.1$. The low solubility of cryptand 2_B.2_B.2 made potentiometric titration unfeasible; however, spectrophotometric titration of 2_B.2_B.2 (8.5×10^{-5} M) at 25 °C yielded an estimate of the second protonation constant, $\log K_{\text{H2}} = 6.2 \pm 0.2$. A value of $\log K_{\text{H1}} = 9.5$ was obtained from solubility experiments at low ionic strength.¹²

Formation Rates at High pH. At pH values in the range 11.0–11.5 cryptands 2_B.2.2 and 2_B.2_B.2 exist predominately in the unprotonated state and the formation reactions may be studied without significant contributions ($\leq 3\%$) from HCry⁺ and H₂Cry²⁺. The metal ion concentration, [M²⁺], used was in excess over the cryptand so that eq 1 would reduce to a pseudo-first-order reaction in the forward direction and a first-order reaction in the reverse direction. Under these conditions, the observed first-order rate constant, k_{obsd} , is the sum of the first-order rate constants for the forward and reverse reactions,²⁶ i.e.

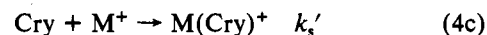
$$-\frac{1}{[\text{Cry}] - [\text{Cry}]_e} \frac{d[\text{Cry}]}{dt} = k_{\text{obsd}} = k_f[\text{M}^{2+}] + k_d \quad (3)$$

Plots of k_{obsd} vs. [M²⁺] were linear (see Figure 2), and values of the second-order formation rate constant, k_f , were obtained from the slope of the appropriate plot. These values are collected in Table I along with the activation parameters. The intercepts of the k_{obsd} vs. [M²⁺] plots are subject to considerable uncertainty, and values of k_d were obtained from separate experiments.

Uncatalyzed Dissociation Rates. The dissociation rates were studied by mixing the cryptate, M(Cry)²⁺, with a scavenger species at high pH^{24,27a}



or



where L = cryptand 2.2.1 or 2.2.2 and M⁺ = Na⁺ or K⁺. Conditions were employed so that $k_s[\text{L}] \gg k_f[\text{Cry}]$ (or $k_s'[\text{M}^+] \gg k_f[\text{M}^{2+}]$) and the overall exchange reactions were

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Table I. Rate Constants and Activation Parameters for Alkaline-Earth Cryptates in Water at 25 °C^a

cryptate	$k_f, \text{M}^{-1} \text{s}^{-1}$	$\Delta H_f^\ddagger, \text{kcal mol}^{-1}$	$\Delta S_f^\ddagger, \text{cal mol}^{-1} \text{deg}^{-1}$	k_d, s^{-1}	$\Delta H_d^\ddagger, \text{kcal mol}^{-1}$	$\Delta S_d^\ddagger, \text{cal mol}^{-1} \text{deg}^{-1}$
Ca(2.2.2) ²⁺ ^b	7.3×10^3	7.9	-14	$0.26 (0.19)^c$	$8.4 (10.8)^c$	-33 (-25.8) ^c
Ca(2 _B .2.2) ²⁺	$(2.4 \pm 0.2) \times 10^3$	12.0 ± 0.7	-3 ± 3	$0.38 \pm 0.02 (0.55)^d$	9.1 ± 0.5	-30 ± 2
Ca(2 _B .2 _B .2) ²⁺	$(1.1 \pm 0.2) \times 10^2$	10.7 ± 3.0	-14 ± 4	0.24 ± 0.2	9.8 ± 1.3	-27 ± 7
Sr(2.2.2) ²⁺ ^b	1.0×10^4	7.4	-15	$1.0 \times 10^{-4} (0.71 \times 10^{-4})^c$	$17.7 (18.9)^c$	-17 (-14.1) ^c
Sr(2 _B .2.2) ²⁺	$(7.3 \pm 0.6) \times 10^3$	10.6 ± 0.7	-5 ± 3	$(3.3 \pm 0.3) \times 10^{-4}$	20.6 ± 0.9	-5 ± 3
Sr(2 _B .2 _B .2) ²⁺	$(2.9 \pm 0.3) \times 10^2$	9.7 ± 0.7	-15 ± 2	$(6.3 \pm 0.2) \times 10^{-4}$	20.1 ± 0.5	-6 ± 1
Ba(2.2.2) ²⁺ ^b	7.0×10^4	6.8	-13	$2.2 \times 10^{-5} (1.8 \times 10^{-5})^c$	$20.9 (21.0)^c$	-9 (-9.8) ^c
Ba(2 _B .2.2) ²⁺	$(7.0 \pm 0.5) \times 10^4$	7.0 ± 0.5	-13 ± 2	$(7.5 \pm 0.6) \times 10^{-4}$	21.5 ± 1.7	0 ± 5
Ba(2 _B .2 _B .2) ²⁺	$(4.6 \pm 0.3) \times 10^3$	10.7 ± 0.8	-6 ± 1	$(1.73 \pm 0.01) \times 10^{-2}$	14.4 ± 2.7	-18 ± 8

^a Ionic strength 0.1 M ((CH₃)₄NCl or (C₂H₅)₄NCl). ^b Reference 24. ^c Reference 2. ^d Reference 26.

Table II. Stability Constants of Alkaline-Earth Cryptates in Water at 25 °C

cryptate	log K_s, M^{-1}	
	kinetic ^a	potentiometric
Ca(2.2.2) ²⁺	4.4 ^b	4.4, ^c 4.6 ^d
Ca(2 _B .2.2) ²⁺	3.8	3.8, ^e 4.0 ^f
Ca(2 _B .2 _B .2) ²⁺	2.66	3.07, ^f 3.4 ^g
Sr(2.2.2) ²⁺		8.0, ^c 8.3 ^d
Sr(2 _B .2.2) ²⁺	7.4	6.9, ^e 7.5 ^h
Sr(2 _B .2 _B .2) ²⁺	5.7	6.3 ^h
Ba(2.2.2) ²⁺		9.5, ^c 9.7 ^d
Ba(2 _B .2.2) ²⁺	8.0	7.4, ^e 7.9 ^h
Ba(2 _B .2 _B .2) ²⁺	5.4 ₃	5.65, ^g 5.6 ₅ ^h

^a From kinetic data, $K = k_f/k_d; I = 0.1 \text{ M}$. ^b Reference 24. ^c Reference 4, $I = 0.05$. ^d Reference 5, $I = 0.1 \text{ M}$. ^e Reference 8. ^f Kolthoff, I. M.; Chantooni, M., Jr., unpublished results. ^g Reference 12, $I = 10^{-3} \text{ M}$. ^h Reference 25.

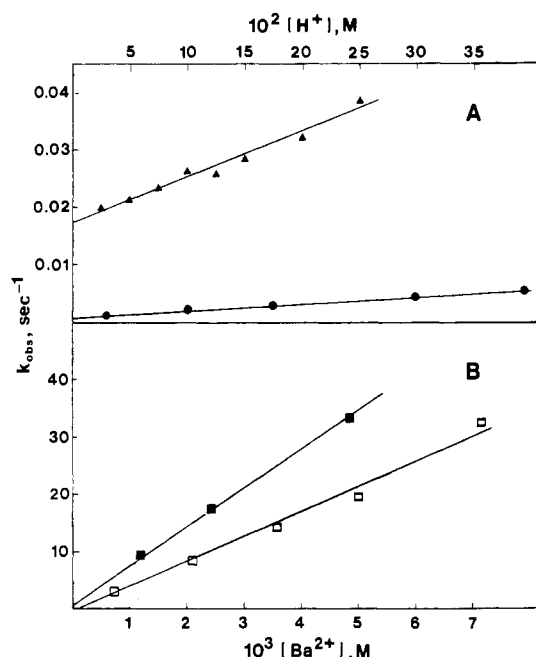


Figure 2. Observed rate constants for barium cryptates at 25 °C: (A) acid-catalyzed dissociation of Ba(2_B.2_B.2)²⁺ (▲) and Ba(2_B.2.2)²⁺ (●); (B) complex formation at pH 11.0–11.5 of Ba(2_B.2_B.2)²⁺ (□) and Ba(2_B.2.2)²⁺ (■, $k_{\text{obsd}}/10$).

irreversible. Under these conditions the first-order rate expression is given by eq 5. The dissociation rates of the Ca²⁺–

$$-\text{d} \ln [\text{M}(\text{Cry})^{2+}] / \text{d}t = k_{\text{obsd}} = k_d \quad (5)$$

Sr²⁺–, and Ba²⁺–2_B.2 cryptates obtained in this manner obeyed first-order kinetics, and the values of k_d were independent of the nature and concentration of the scavenger species. More detailed studies of Ca(2_B.2.2)²⁺ at 25 °C also

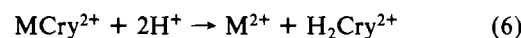
Table III. Rate Constants and Activation Parameters for Proton Catalysis of Alkaline-Earth Cryptates in Water at 25 °C

cryptate	$k_{\text{H}^+}^a, \text{M}^{-1} \text{s}^{-1}$	$\Delta H_{\text{H}^+}^\ddagger, \text{kcal mol}^{-1}$	$\Delta S_{\text{H}^+}^\ddagger, \text{cal mol}^{-1} \text{deg}^{-1}$	$k_{\text{H}^+}/k_d, \text{M}^{-1}$
Ca(2.2.2) ²⁺ ^b	550			2600
Ca(2 _B .2.2) ²⁺	$(1.56 \pm 0.07) \times 10^3$	15.1 ± 2.2	+7 ± 1	4100
Ca(2 _B .2 _B .2) ²⁺	133 ± 3	12.4 ± 0.8	-7 ± 1	550
Sr(2.2.2) ²⁺ ^b	0.0213			280
Sr(2 _B .2.2) ²⁺	0.134 ± 0.009	12.1 ± 0.7	-22 ± 3	410
Sr(2 _B .2 _B .2) ²⁺	0.212 ± 0.011	8.8 ± 0.9	-32 ± 8	340
Ba(2.2.2) ²⁺ ^b	1.4×10^{-3}			80
Ba(2 _B .2.2) ²⁺	$(4.9 \pm 0.1) \times 10^{-2}$	13.9 ± 0.6	-18 ± 2	65
Ba(2 _B .2 _B .2) ²⁺	0.31 ± 0.02	11.6 ± 0.6	-22 ± 2	18

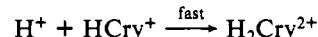
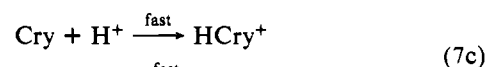
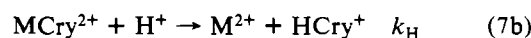
^a Values refer to infinite dilution in water. ^b Reference 27.

revealed that the value of k_d was insensitive to the ionic strength (0.08–0.52 M, Me₄NCl–Me₄NOH). The dissociation rate constants for Ca(2_B.2_B.2)²⁺ and Sr(2_B.2_B.2)²⁺ were obtained by similar procedures using Na⁺ and cryptand 2.2.2 as scavengers, respectively. All reactions obeyed first-order kinetics as described by eq 5 and were independent of the nature and concentration of the scavenger. The dissociation rate constants of Ba(2_B.2_B.2)²⁺ were obtained from the intercepts of plots of k_{obsd} vs. [H⁺] (vide infra) except for those at 25 °C. These values were also obtained at high pH with use of cryptand 2.2.2 as the scavenger for Ba²⁺. In this case the value of k_d obtained (0.0174 ± 0.0002) was independent of scavenger concentration and was in excellent agreement with the value obtained (0.0173 ± 0.0003) with use of [H⁺] to promote the dissociation reaction. The values of the dissociation rate constants at 25 °C and the corresponding activation parameters are listed in Table I.²⁵

Acid-Catalyzed Dissociation Rates. Hydrogen ion may also be used as a scavenger to study the dissociation rates of cryptates^{27b} with the overall reaction given by eq 6. However,



as reported for other cryptate systems,^{9–11,27b,28} the observed first-order rate of dissociation was found to have a first-order dependence on [H⁺]. Equations 7a–7c represent the reactions



in the presence of excess acid. If the steady-state approximation for [Cry] and [HCry⁺] is invoked, the rate law given by eq 8 is obtained. Plots of k_{obsd} vs. [H⁺] were linear (see

$$\frac{1}{[\text{MCry}^{2+}]} \frac{d[\text{MCry}^{2+}]}{dt} = k_{\text{obsd}} = k_d + k_H[\text{H}^+] \quad (8)$$

Figure 2), and the slope of the line yielded the value of the second-order rate constant, k_H . The intercepts of these plots for the $\text{Ba}(\text{2}_B\text{-2}_B\text{-2})^{2+}$ system yielded values of k_d at the temperature studied. For the other cryptate systems the intercepts gave only approximate values of k_d . The values of k_H obtained at an ionic strength of 0.1 M were corrected to zero ionic strength with use of eq 9,²⁹ where the activity coefficients were

$$k_H/k_H(I=0) = f_{\text{H}^+}f_{\text{MCry}^{2+}}/f_{(*)} \quad (9)$$

calculated by using the Davies equation.³⁰ The corrected values of k_H at 25 °C and their respective activation parameters are listed in Table III.

Discussion

The stability constants and the complexation selectivity of the cryptands may be altered by systematic variation of the following structural parameters: (i) number and type of donor atoms, (ii) cavity size and geometry, and (iii) layer properties.⁷ The cryptands studied all contain eight donor atoms (2 N, 6 O); however, the catechol-type oxygens of the benzo cryptands are less effective donor atoms than the aliphatic ether oxygens. This should result in a decrease in complex stability for all cations as benzene moieties are incorporated into the cryptand. The addition of benzo rings decreases the flexibility of the ligand by eliminating rotation around the central C-C bond of the polyether bridge, leading to a decrease in the effective cavity size. Indeed, the N...N distance of uncomplexed $\text{2}_B\text{-2}_B\text{-2}$ is $5.161 \pm 0.002 \text{ \AA}$ ³¹ in the solid state, which is at the lower end of the range of N...N distances found (4.92–6.07 Å) for a series of 2.2.2 cryptates³² and less than the N...N distance of 5.441 Å found for $\text{Ca}(\text{2.2.2})\text{Br}_2$.³³ The diminution of cavity size would be expected to favor Ca^{2+} over Sr^{2+} and Ba^{2+} . The lipophilic benzo rings also increase the overall thickness of the organic "skin" of the complex, which should decrease interaction between the solvent and the complexed cation. This shielding effect should lower all stability constants and has been cited as one factor responsible for the systematic decrease of divalent/monovalent cation selectivity for the Ba^{2+} and K^+ complexes of $\text{2}_B\text{-2.2}$ and $\text{2}_B\text{-2}_B\text{-2}$.⁸

The second column of Table II contains values of the stability constants obtained by combining the k_f and k_d values ($K_s = k_f/k_d$), and the third column lists values from potentiometric titrations.^{8,12} The calculated values for Ca^{2+} with $\text{2}_B\text{-2.2}$ and $\text{2}_B\text{-2}_B\text{-2}$ and Ba^{2+} with $\text{2}_B\text{-2}_B\text{-2}$ are in reasonable agreement with the corresponding values from titration experiments. The agreement for the other systems is only fair. The differences for the $\text{2}_B\text{-2}_B\text{-2}$ cryptates are in part due to the higher ionic strength employed for the kinetic studies and are consistent with the finding that $\gamma_{\text{ML}^{2+}} > \gamma_{\text{M}^{2+}}$, where L = $\text{2}_B\text{-2}_B\text{-2}$.¹²

The stepwise introduction of the benzo rings decreases the stability constant values by ~40-, 200-, and 10^4 -fold for Ca^{2+} , Sr^{2+} , and Ba^{2+} , respectively, in going from 2.2.2 to $\text{2}_B\text{-2}_B\text{-2}$. For a given metal ion, the addition of each benzo group decreases the K_s value by roughly the same factor. The relatively small changes for the Ca cryptates may be due to the opposing

effects of decreased cavity size and lower donor atom basicity and cryptate solvation. In the case of the larger Ba^{2+} , the decrease in cavity size also acts to destabilize the cryptates. The complexation selectivity sequences change from $\text{Ba} > \text{Sr} \gg \text{Ca}$ to $\text{Ba} \approx \text{Sr} \gg \text{Ca}$ to $\text{Sr} \approx \text{Ba} > \text{Ca}$ for 2.2.2, $\text{2}_B\text{-2.2}$, and $\text{2}_B\text{-2}_B\text{-2}$, respectively. Thus, it appears that the cavity of $\text{2}_B\text{-2}_B\text{-2}$ is decreased to a size that most readily accommodates Sr^{2+} . A similar shift in complexation selectivity has been reported for alkali-metal ion-benzo cryptates in propylene carbonate.¹¹ However, specific solvent effects may also play a role since no change in the order of selectivity was noted for a similar study in methanol.¹⁰ It is also of interest to note that the range of stability constants for a given cryptand decreases from ~ 10^5 (Ba/Ca) for 2.2.2 to 400 (Sr/Ca) for $\text{2}_B\text{-2}_B\text{-2}$. This trend supports the idea of a decreased cavity size for $\text{2}_B\text{-2.2}$ and $\text{2}_B\text{-2}_B\text{-2}$ since the K_s values for alkaline-earth ions with the smaller cryptand 2.2.1 vary by a factor of 11.⁴

Formation Rate Constants. The cryptate formation reactions are second-order processes in the concentration range studied. For each metal ion the introduction of the first benzo ring results in a small decrease in the k_f value. The introduction of the second benzo ring results in a further, but larger, decrease in k_f , about 20-fold for all metal ions.

For each cryptand the order of reactivity $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+}$ parallels the predicted solvent-exchange rates of the metal ions.³⁴ The previously reported k_f values for the cryptand 2.2.2 are many orders of magnitude lower than those of complexation reactions with acyclic ligands and macrocyclic polyethers.³⁵ This has been attributed to a very low concentration of the reactive form of the cryptand in solution and/or steric control which shifts the rate-determining step to one subsequent to first bond formation and may require multiple desolvation of the metal ion.^{24,36} The introduction of the benzo rings increases the rigidity of the ligand, making it more difficult for stepwise solvent replacement to occur. It seems unlikely that first bond formation involves a tertiary nitrogen atom, and one or more intermediates with the cation bonded to bridge oxygen atoms are formed prior to formation of the transition-state complex. The benzo rings provide increased steric hindrance to these potential binding sites, and the lower basicity of the catechol oxygens, relative to that of the aliphatic ether oxygens, would tend to decrease the steady-state equilibrium concentrations of any reaction intermediates. Comparison of the activation parameters for the complex formation reactions of cryptands 2.2.2, $\text{2}_B\text{-2.2}$, and $\text{2}_B\text{-2}_B\text{-2}$ reveals that an increase in the enthalpy of activation is the predominant factor in the decrease of the k_f values from 2.2.2 to $\text{2}_B\text{-2.2}$. This is consistent with increased difficulty of stepwise solvent substitution as the ligand is made more rigid by introduction of successive benzo rings.

Dissociation Rate Constants. The dissociation rate constants exhibit a more varied pattern as shown in the lower portion of Figure 3. The k_d values are almost constant for the Ca complexes while those for the Sr and Ba cryptates increase monotonically with the introduction of successive benzo rings. The reactivity sequences for a given cryptand change from $\text{Ca} \gg \text{Sr} > \text{Ba}$ for 2.2.2 to $\text{Ca} > \text{Ba} > \text{Sr}$ for $\text{2}_B\text{-2}_B\text{-2}$, the Sr/Ba crossover occurring with $\text{2}_B\text{-2.2}$. To a large extent the pattern of k_d values is a mirror image of the pattern of stability constant values. The observed changes of the k_d values are related to the ratio of cryptand cavity size to cation radius and the increasing internal strain of the complexes as benzo rings

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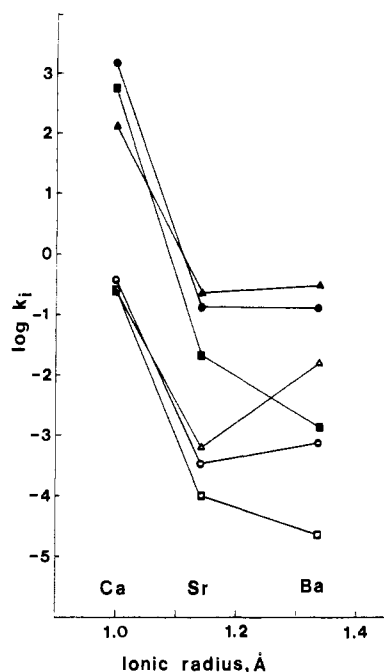


Figure 3. Uncatalyzed and acid-catalyzed dissociation rate constants at 25 °C vs. ionic radius (solid symbols, $\log k_H$; open symbols, $\log k_d$): (squares) 2.2.2; (circles) $2_B.2_B.2$; (triangles) $2_B.2_B.2$.

are added. The former property would tend to stabilize the Ca cryptates and destabilize the Ba and, to lesser extent, the Sr cryptates, while the latter would be expected to result in an increase in k_d values. Increased substitution on the carbon backbone on many chelating ligands has been shown to increase the dissociation rate constants of their metal ion complexes.³⁷ For the Ca complexes the two effects appear to cancel each other, resulting in the relatively constant values of k_d . However, for the Sr and Ba cryptates both effects would act to increase the k_d values on going from 2.2.2 to $2_B.2_B.2$. The k_d values for the $\text{Sr}(2.2.1)^{2+}$ and $\text{Ba}(2.2.1)^{2+}$ cryptates, 1.45×10^{-3} and $6.4 \times 10^{-2} \text{ s}^{-1}$, respectively,²⁷ support this explanation since the cavity diameter of cryptand 2.2.1 is estimated to be 0.6 Å less than that of the cryptand 2.2.2.⁷

The activation parameters for k_d , listed in Table I, are shown in the form of an isokinetic plot in Figure 4. For the Ca cryptates, ΔH_d^\ddagger and ΔS_d^\ddagger contribute equally to the free energy of activation with the slight increase in the enthalpy of activation offset by the increase in entropy of activation. The ΔH_d^\ddagger values for the Sr and Ba cryptates are much larger than those for Ca, reflecting the tighter fit of the cation into the cryptand cavity. The ΔS_d^\ddagger values for the Ca cryptates are generally more negative than the corresponding values for Sr and Ba cryptates, consistent with the idea that the metal ion is highly solvated in the activated complex.^{24,38} For a given metal ion the ΔS_d^\ddagger values generally become less negative as successive benzo rings are added. This trend may arise from differences in solvation of the cryptand donor atoms in the transition state, with the catechol oxygen atoms less strongly solvated than the aliphatic ether type oxygens.¹² The more highly strained benzo cryptates may also gain more internal entropy as they proceed to the transition-state complex as proposed for the dissociation of alkali-metal ion cryptates in methanol.¹⁰ The activation parameters for $\text{Ba}(2_B.2_B.2)^{2+}$ do not fit the general pattern, however; preliminary results from an X-ray diffraction study³⁹ indicate that the conformation

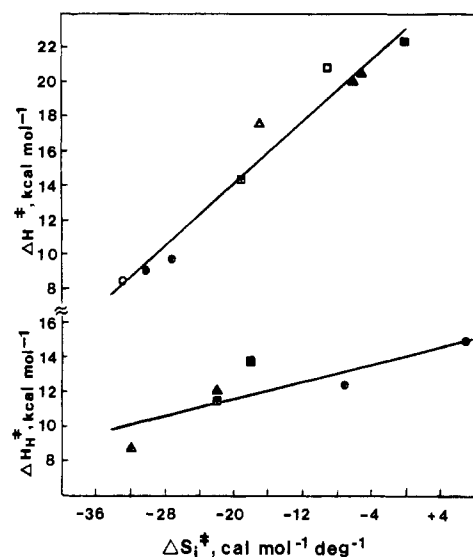


Figure 4. ΔH^\ddagger vs. ΔS^\ddagger for the uncatalyzed and proton-catalyzed dissociation of Ca (circles), Sr (triangles), and Ba (squares) cryptates in H_2O : (open symbols) 2.2.2; (solid symbols) $2_B.2_B.2$; (crosshatched symbols) $2_B.2_B.2$.

of the complexed ligand is similar to that of dibenzo-18-crown-6 complexed with K^+ ⁴⁰ with both benzo rings bent back toward the aliphatic bridge, leaving the Ba ion more exposed on one side. The Ca^{2+} - and Sr^{2+} - $2_B.2_B.2$ cryptates may have similar conformations although these smaller cations may be situated more deeply in the ligand cavity and thus less accessible to the solvent. Although the activation parameters vary over a wide range of values, the data shown in Figure 4 suggest an isokinetic relationship indicative of a common reaction mechanism. A similar isokinetic relationship has been reported for the dissociation in methanol of alkaline-earth complexes of monocyclic analogues of the cryptand 2.2.2.⁴¹

Proton-Catalyzed Dissociation Rate Constants. The variation of the values of k_H listed in Table III is shown in the upper part of Figure 3. The values for the Ca cryptates are generally 3–4 orders of magnitude larger than those for the Sr and Ba cryptates. The reactivity pattern is similar to that of the corresponding k_d values also shown in Figure 3. The greater reactivity of the Ca cryptates may be related to the poor fit of the smaller Ca^{2+} ion in the cryptand cavity, making it easier for the cryptate to adopt the endo-exo conformation prior to proton attack. On the other hand, if proton attack occurs to the endo-endo cryptate conformation, it may be easier for a proton to enter the cavity containing the smaller Ca^{2+} ion, however; the higher charge density and lower polarizability of Ca^{2+} relative to that of Sr^{2+} or Ba^{2+} would tend to offset the steric advantage. The ratios of k_H/k_d , listed in Table III, fall into distinct groups governed by the central metal ion, with only minor variations among the three ligands. Assuming that the mechanism for the uncatalyzed dissociation is similar for all complexes, it appears that proton attack occurs earlier in the dissociation process of the Ca cryptates than for those of Sr and Ba. The activation parameters for the acid-catalyzed dissociation fall into two distinct groups when compared with the activation parameters for k_d . For the Ca cryptates $\Delta H_H^\ddagger > \Delta H_d^\ddagger$ and ΔS_H^\ddagger is more positive than ΔS_d^\ddagger

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whereas the opposite is true for the Sr and Ba cryptates. These trends are consistent with a mechanism where proton attack occurs before the Ca ion is highly solvated as proposed for the uncatalyzed dissociation reaction.²⁴ The proton may also undergo desolvation to a greater degree with the Ca complexes, leading to a more positive entropy of activation relative to that for the Sr and Ba cryptates. Lowered solvation of Ca²⁺ ion (and the cryptand) along with electrostatic repulsion would tend to increase ΔH_H^\ddagger relative to ΔH_d^\ddagger . For the Sr and Ba cryptates proton attack may occur later in the dissociation process. This would allow greater solvation of the metal ion and cryptand, and the proton may require less desolvation to react with the exposed bridgehead nitrogen. The tighter fit of the Sr and Ba cations into the cryptand cavity may also result in greater steric strain in the protonated transition state, resulting in more negative values of ΔS_H^\ddagger relative to those for the Ca cryptates. The observed activation parameters suggest either (i) that the Ca cryptate cavity is more accessible to the proton than the Sr and Ba cryptates or (ii) that the Ca cryptates undergo endo-endo to endo-exo isomerization more readily than the cryptates of the larger Sr and Ba ions.

Conclusions

The introduction of two successive benzo rings to the cryptand 2.2.2 results in a progressive decrease in stability constants with the alkaline-earth cations. The complexation selectivity patterns change from Ba > Sr >> Ca to Ba \approx Sr >> Ca and Sr \approx Ba > Ca for 2.2.2, 2_B.2.2, and 2_B.2_B.2, respectively, due to decreasing cavity size. As benzo rings are added, the formation rate constants decrease for each metal

ion due to the increasing steric barriers and cryptand rigidity. The dissociation rate constants change in a more complex manner; those for the Ca cryptates remain almost constant while those for the Sr and Ba cryptates increase by ~ 6 -fold and ~ 800 -fold, respectively, as successive benzo rings are added.

The contraction of cavity size tends to oppose the effects of decreased donor atom strength and increased ligand thickness and rigidity for the Ca cryptates while all these factors work to accelerate the cryptate decomposition rates of Sr and Ba as successive benzo rings are introduced. All of the cryptates exhibit proton-catalyzed dissociation with the relative extent of catalysis increasing in the order Ba < Sr < Ca for a given ligand. The ability of the cryptate to achieve a conformation accessible to proton attack (endo-exo) or for the proton to partially penetrate the cryptate cavity appears to be inversely proportional to the size of the complexed alkaline-earth cation.

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Registry No. 2.2.2, 23978-09-8; 2_B.2.2, 31250-18-7; 2_B.2_B.2, 40471-97-4; Ca(2.2.2)²⁺, 32614-34-9; Ca(2_B.2.2)²⁺, 80679-40-9; Ca(2_B.2_B.2)²⁺, 87635-44-7; Sr(2.2.2)²⁺, 32614-35-0; Sr(2_B.2.2)²⁺, 91760-57-5; Sr(2_B.2_B.2)²⁺, 91760-58-6; Ba(2.2.2)²⁺, 61624-62-2; Ba(2_B.2.2)²⁺, 91780-98-2; Ba(2_B.2_B.2)²⁺, 80712-58-9; Ca, 7440-70-2; Sr, 7440-24-6; Ba, 7440-39-3.

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Gas-Solid Interactions of Zinc Tetraphenylporphine with Various Volatile Ligands¹

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The gas-solid adsorptions of organic compounds (primarily amines) with zinc tetraphenylporphine (ZnTPP) coated on thermalized carbon black have been probed by measuring the temperature dependence of the gas chromatographic retention volumes. The derived free energies, enthalpies, and entropies of adsorption are reported. Approximately the same order of binding for major classes of ligands (N > P > O \approx S) is found in this solvent-free system as that observed for ZnTPP in cyclohexane. However, the detailed study of the adsorption using physical organic models reveals a number of differences when compared to that of solvated systems. The entropy and enthalpy of adsorption appear to be significantly correlated for a wide range of organic ligands including hydrocarbons and all of the heteroatom compound types listed here.

Introduction

Metalloporphyrin chemistry has been intensively studied for a number of years because of its intrinsic interest and the similarity of these compounds to the active sites in hemoglobin, chlorophyll, and other biologically important molecules.⁴ The complexes of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (H₂TPP) have frequently been used because of their ease of preparation and solubility in organic solvents.⁵ The Zn²⁺ complex of H₂TPP is especially useful because it forms a variety of pentacoordinate d¹⁰ complexes in which the fifth ligand site is occupied by various Lewis bases. Because of the stable electronic configuration, there is essentially no ligand to metal π bonding and the complexes do not readily undergo redox processes. Thus, even such novel ligands as the superoxide ion can be used.⁶

We have recently explored the use of ZnTPP adsorbed onto graphitized carbon black as an adsorbent for amines in packed-column gas-solid chromatography.^{3,7} In the course of these studies we have obtained considerable information on the thermodynamics of the absorption processes, which we report here and compare to solution-phase data for similar complex formation.

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